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INTERFERENCE OF OXYGEN, CARBON DIOXIDE,
AND WATER VAPOR ON THE ANALYSIS FOR
OXIDES OF NITROGEN BY CHEMILUMINESCENCE

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SUMMARY

The interference of small concentrations (less than 4 percent by volume) of oxygen, carbon dioxide, and water vapor on the analysis for oxides of nitrogen by chemiluminescence has been measured. The sample gas consisted primarily of nitrogen, with less than 100 parts per million concentration of nitric oxide, and with small concentrations of oxygen, carbon dioxide, and water vapor added. Results obtained under these conditions indicate that although oxygen does not measurably affect the analysis for nitric oxide, the presence of carbon dioxide and water vapor causes the indicated nitric oxide concentration to be too low. An interference factor – defined as the percentage change in indicated nitric oxide concentration (relative to the true nitric oxide concentration) divided by the percent interfering gas present – was determined for carbon dioxide to be -0.60 ± 0.04 and for water vapor to be -2.1 ± 0.3 .

INTRODUCTION

Few methods of quantitative analysis for a specific constituent in a gas mixture are completely straight-forward and without complications introduced by the presence of foreign gases or other factors. The quantitative analysis of nitric oxide (NO) and nitrogen dioxide (NO₂) by the relatively newly commercially developed method of chemiluminescence is no exception. Although this method is very attractive because of its ease, speed, and sensitivity (concentrations as low as 1 part per billion (ppb) or even lower can be measured), the method does suffer from limitations of foreign gas interference – in spite of the fact that the method was developed as one which would be essentially free of such interferences. Although great progress has been made in this direction, such interferences are nevertheless not negligible, and should therefore be taken into account when making quantitative measurements intended as other than merely rough estimates.

The present paper presents the results of such interference measurements on gas samples consisting of up to 4 percent (by volume) oxygen, up to 3.5 percent carbon dioxide, and up to 1.8 percent water vapor (dewpoint 16.1° C) in a balance gas of nitrogen containing nitric oxide concentrations up to 90 parts per million (ppm). These particular

concentrations are of interest because they occur in the air oxidation of hydrocarbons after the product gases have been diluted with a large quantity of nitrogen.

SYMBOLS AND ABBREVIATIONS

$h\nu$	quantum of light
I	signal intensity of chemiluminescent emission, arbitrary units
i_F	interference factor defined by equation (6)
k	rate constant associated with the reactions in equations (1) to (4)
M	unspecified third-body molecule
P	total ambient pressure, torr (1 torr = 0.133 kN/m ²)
p	vapor pressure, torr (1 torr = 0.133 kN/m ²)
x	mole fraction
y	species concentration, ppm
z	species concentration, volume percent
Δy	$y_{ind} - y_{calc}$
$\Delta y'$	Δy adjusted to eliminate bias due to errors in measurements
[]	concentration of species within the brackets, unspecified units

Subscripts:

act	actual
calc	calculated from flow rate mixing
dil	diluent gas

ind indicated by C/L-A before correction

Abbreviations:

C/L-A chemiluminescent analyzer or analysis

cal calibration

dil diluent gas or dilution

FM flowmeter

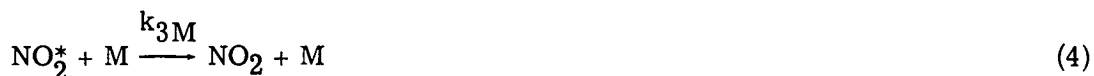
sccm standard cubic centimeters per minute

TC thermocouple

An asterick * refers to activated state.

BACKGROUND

In the quantitative analysis for NO and NO₂ by chemiluminescence, foreign gases (i.e., gases present in the sample which are not present in the calibration gas) can interfere with the analysis to produce an indicated concentration which is in error. These foreign gas interferences can arise from a variety of sources such as changes in gas viscosity affecting sample gas flow rates, chemiluminescence of other chemical species in the same spectral region as the nitric oxide-plus-ozone chemiluminescence (red and near infra-red), quenching reactions from third-body molecules, and perhaps other sources as well. Interferences caused by changes in gas viscosity are likely to be negligible unless substantial quantities of foreign gas are present, or unless the foreign gas in the sample stream has a viscosity sufficiently different from that of the calibration gas to cause a significant difference in sample gas viscosity from the calibration gas viscosity. Interferences caused by the chemiluminescence of other chemical species is conventionally kept small in commercial chemiluminescent analyzers (designated C/L-A's) by a judicious choice of spectral filters and photodetectors designed to limit that portion of the spectrum observed to a band specific for nitric oxide-plus-ozone chemiluminescence. However, interferences caused by quenching reactions from foreign gas molecules are unavoidable because of the very nature of the reaction mechanism for nitric oxide-plus-ozone chemiluminescence (see refs. 1 and 2):



where, under the usual conditions of operation (20° C and several torr), $k_2 \ll k_{3\text{M}}[\text{M}]$. Reaction (4) is in direct competition with reaction (3), which is the step responsible for the photoemission. The relative rates of reactions (3) and (4) depend largely on the concentration of the third-body molecule $[\text{M}]$, and on the nature of the third-body molecule, which determines the precise value of $k_{3\text{M}}$; however, typically, k_2 is very small with respect to $k_{3\text{M}}[\text{M}]$. For this condition, the chemiluminescent emission I is directly proportional to the nitric oxide concentration, that is

$$I = \frac{k_1^* k_2}{k_{3\text{M}}} \frac{[\text{NO}][\text{O}_3]}{[\text{M}]} \quad (5)$$

But this competition of reaction (4) with reaction (3) also establishes the importance of the nature and concentration of the third-body molecule in determining the magnitude of the chemiluminescent emission I . Clyne, Thrush, and Wayne (ref. 1) have measured values of relative quenching efficiency $k_{3\text{M}}/k_{3\text{O}_2}$ for a selected number of gases and these are reproduced in Table I.

TABLE I.- RELATIVE QUENCHING EFFICIENCY $k_{3\text{M}}/k_{3\text{O}_2}$
OF SELECTED GASES

Ar	O ₂	N ₂	H ₂	N ₂ O	NO ₂
0.5	1.0	0.9	1.2	2.6	14.0

As would be expected, the greater the number of degrees of freedom in a molecule, the greater is its quenching efficiency. Since oxygen and nitrogen have approximately the

same quenching efficiency, the presence of oxygen in a nitric oxide in nitrogen sample would be expected to cause negligible interference relative to a calibration gas of nitric oxide in pure nitrogen. But not reported in reference 1 are the quenching efficiencies of the two triatomic molecules, carbon dioxide and water vapor, that are so important in hydrocarbon combustion. From the data for other triatomic molecules in table I, these could be potentially very large, indeed. This implies that a sample gas whose composition is different from that of a calibration gas will, even for the same nitric oxide concentration, produce a different level of chemiluminescent emission, that is, unless the quenching efficiencies of the sample and calibration gases fortuitously are the same.

Since to account for quenching interferences by calculation would not only be tedious but highly uncertain because of possible interferences from other causes, the magnitude of the total interference for each foreign gas expected should be measured relative to the calibration gas, and the indicated nitric oxide concentration in any analysis corrected for this interference.

EXPERIMENTAL APPARATUS

The experimental apparatus, shown schematically in figure 1, consisted of a flow-mixing system for diluting nitric oxide calibration gas with up to 4 percent nitrogen, oxygen, or carbon dioxide, and also of a means of humidifying the calibration gas. The calibration gases employed were 13 ppm \pm 1.3 ppm nitric oxide in nitrogen, and 90 ppm \pm 5.4 ppm nitric oxide in nitrogen, supplied and certified by Air Products and Chemicals, Inc. The diluent gases were 99.998 percent nitrogen with a dewpoint of less than -67.8° C, 99.5 percent oxygen with a dewpoint of less than -62.2° C, and 99.5 percent carbon dioxide with a dewpoint of less than -40.0° C. Flow rates were measured with calibrated linear mass flowmeters; each flowmeter was checked and recalibrated several times during the course of the experiments with a soap-film calibration unit. Gas flow rates were controlled with very fine control needle valves, and gas cylinder delivery pressures were suitably regulated so that there was no flow instability or drift. All analyses for NO and NO₂ were performed with the ThermoElectron Corporation Model 12A NO-NO_x Chemiluminescent Analyzer.

The humidification system consisted of a heated, 1 liter 3-neck, round-bottom flask above which were mounted two condensers in series. A tube for the introduction of a carrier gas extended into the flask below the water level and was perforated at the tip. The heating mantle and the three heating coils (see fig. 1) were controlled independently with autotransformers. Temperatures were measured with chromel-alumel thermocouples at the points noted in figure 1 and were recorded on a multipoint automatic temperature referencing recorder. Thermocouple 1 was located in the water in the flask, thermocouple 2 was taped to the exterior of the ground glass joint between the two con-

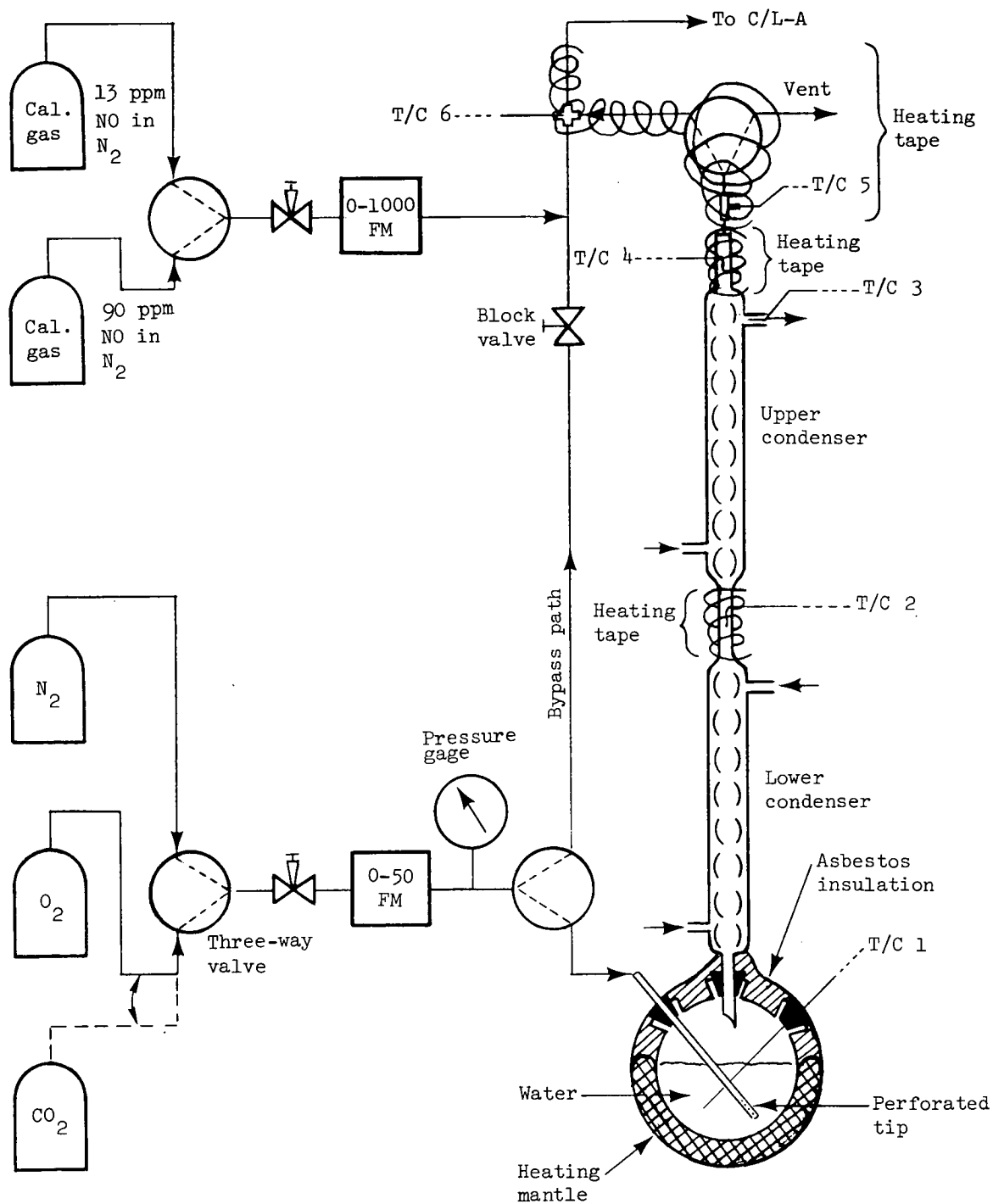


Figure 1.- Experimental apparatus.

densers, thermocouple 3 was located in the exit stream of cooling water, thermocouple 4 was taped to the exterior of the wall at the exit of the upper condenser, and thermocouples 5 and 6 were located in the humid gas stream. Cooling water to the condensers was supplied from separate, individually thermostated heat baths, the temperatures of which were read with mercury immersion thermometers. The transfer lines for all gas streams containing nitric oxide were primarily of teflon, although some small amount of stainless steel was used; the valves and fittings were either teflon or stainless steel. As indicated in appendix A, this particular choice of materials is of little consequence.

EXPERIMENTAL PROCEDURE

Oxygen and Carbon Dioxide Interference

For measuring the interference of oxygen and carbon dioxide, the humidification column was bypassed and oxygen or carbon dioxide was flow-mixed with nitric oxide calibration gas in the appropriate flow-rate ratios to give the desired oxygen or carbon dioxide concentrations, and the resulting gas mixtures were analyzed for nitric oxide by C/L-A. Nitrogen, by itself, was also flow-mixed with the nitric oxide calibration gas to serve as a check on the flow-mixing technique.

Water Vapor Interference

For measuring the interference of water vapor, nitric oxide calibration gas was humidified by adding to it a saturated stream of nitrogen and analyzing the resulting humid gas stream for nitric oxide. To saturate the nitrogen carrier gas, it was bubbled through water at 85° C in the flask, flowed upwards through the lower condenser whose walls were held at 79° C, and finally through the upper condenser whose walls were maintained at 70° C. Considerable condensate from the nitrogen carrier stream formed on the walls throughout the entire length of the lower condenser, whereas only a fine mist condensed on the walls in the lower half of the upper condenser, and none at all in the upper half. Hence, the nitrogen carrier stream should closely approach saturation at the temperature of the exiting cooling water from the upper condenser, typically 68.9° C. The exit region of the upper condenser, the transfer lines from the upper condenser to the mix point with the calibration gas, and the ground-glass joint between the two condensers were all held at temperatures well above 70° C to prevent condensation at these points. Typically, temperatures during a humidification run were: flask water, 85° C; thermocouple 2, 96° C; TC 3, 68.9° C; TC 4, 89° C; TC 5, 90° C; TC 6, 85° C (sometimes as low as 57° C with nitric oxide calibration gas flowing); lower condenser water bath, 79° C; and upper condenser water bath, 70° C. The desired water-vapor concentrations in the sample stream to the C/L-A were obtained by appropriately adjusting the flow rates of the nitric oxide calibration gas and the nitrogen carrier gas to the flask-and-

condenser column. The maximum dewpoint of the calibration gas stream thus humidified was kept below 17° C, and therefore from the mix point to the C/L-A, all transfer lines were at room temperature.

As a check on the accuracy of this humidification method, pure nitrogen was substituted for the nitric oxide calibration gas and was humidified as described. The humidity of the resulting nitrogen test stream was measured with a dewpoint hygrometer. For the average of six runs at different flow rates of nitrogen carrier gas through the condenser column, these humidity measurements indicated that the nitrogen carrier gas would have to have been saturated at 68.4° C, whereas the average of the condenser cooling-water exit temperature was 68.9° C. Since a 0.5° C temperature drop from the cooling water side of the condenser wall to the saturated nitrogen carrier gas side appears to be reasonable, for all humidity calculations it was assumed that the nitrogen carrier gas was saturated at 68.4° C, that is, the partial pressure of water vapor in the saturated nitrogen carrier gas was 218.0 torr. In the actual experiments to measure water-vapor interference, the nitrogen carrier gas was, on alternate runs, directed up the condenser column and around the condenser column prior to its mixing with the nitric oxide calibration gas. This arrangement provided a reference for the accuracy of the flow-mixing technique. Runs were also made with oxygen in place of nitrogen as the carrier gas.

Analysis of Sample Gas Nitric Oxide by the Chemiluminescent Analyzer

Since the response of the C/L-A is weakly dependent on the supply pressure of the sample, the sample pressure was held constant at atmospheric pressure by providing excess sample to the input port of the C/L-A, this excess being vented to the atmosphere. For determining the (indicated) nitric oxide concentration of a sample, readings of pure calibration gas were alternately made between readings of the same calibration gas diluted by the particular gas under investigation for its interference effects. This frequent switching to calibration gas was necessitated by slow, long-term drift in the C/L-A readings. (It should be appreciated that for this technique to be effective, nitric oxide calibration gas concentration must be close to that of the sample gas; otherwise, this switching produces significant adsorption and desorption lag in the transfer lines.)

In all cases, data were taken in both the NO and NO_x modes. In the latter mode, prior to entering the NO + O₃ reactor, the sample stream is directed through a stainless-steel catalytic converter coil at 800° C to effect thermal conversion of any nitrogen dioxide in the sample to nitric oxide to permit subsequent detection. Since no nitrogen dioxide was present in the samples, the C/L-A readings were virtually the same for the two modes, and only those data for the NO mode are reported. However, since deconditioning of the stainless-steel catalyst coil can easily occur in an application such as the present

one in which the oxygen concentration of the stream is very small, adequate precautions must be taken to guard against such deconditioning, particularly when an accurate analysis for nitrogen dioxide is important. This phenomenon of deconditioning is discussed in more detail in appendix B.

RESULTS AND DISCUSSION

The experimental data and selected parameters calculated from these data for determining the magnitude of the interference effect are shown in table II for oxygen and carbon dioxide, and in table III for water vapor. In the first six columns are listed the concentration of the calibration gas, the diluent gas under investigation for its interference effect, the flow rates of the calibration and diluent gases, and the calculated concentrations of nitric oxide and diluent in the resulting sample gas. In the seventh and eighth columns of tables II and III are listed the indicated nitric oxide concentration in the stream as measured by the C/L-A (by using the undiluted calibration gas itself as the calibration gas), and the difference between the indicated nitric oxide concentration and the calculated nitric oxide concentration Δy_{NO} . For dilution with nitrogen, Δy_{NO} should, of course, be zero, and any difference from zero suggests the presence of errors in measuring the calibration-gas or diluent-gas flow rates, or in measuring the nitric oxide concentration by the C/L-A. To eliminate this bias, in table II all Δy_{NO} values were adjusted by the average of the Δy_{NO} values obtained for dilution with nitrogen, and in table III, where a carrier gas was used, the adjustment was made relative to the carrier gas in those runs in which it bypassed the condenser column. This adjusted value of Δy_{NO} is listed in tables II and III as $\Delta y'_{\text{NO}}$. An interference factor defined as

$$i_F = \frac{(\Delta y'_{\text{NO}})100}{y_{\text{NO}}^z} \quad (6)$$

is given in the last column of tables II and III, where z is the concentration (in percent) of the interfering species, and i_F is in units of percent error in indicated nitric oxide concentration per percent of foreign gas present.

In table II, only an interference factor for carbon dioxide has been calculated, since, from these data, the interference factor for oxygen is clearly zero. These results imply that carbon dioxide is more efficient as a third body in quenching NO_2^* than is nitrogen, and that oxygen has a quenching efficiency very close to that of nitrogen. These results are consistent with the relative quenching efficiencies of Clyne, Thrush, and Wayne (ref. 1) reproduced in table I. For carbon dioxide, although the mean of i_F for the 13-ppm nitric oxide runs is slightly lower than the mean of i_F for the 90-ppm nitric oxide runs, a statistical comparison of these means indicates that the difference is not

TABLE II. - INTERFERENCE OF OXYGEN AND CARBON DIOXIDE

NO calibration gas concentration, ppm	Diluent gas	Flow rate, sccm		Calculated concentration		$y_{NO, ind}'$ ppm	$\Delta y_{NO} = y_{NO, ind} - y_{NO, calc}$	$\Delta y_{NO}'$ ppm	$i_F = \frac{\Delta y_{NO}' \cdot 100}{y_{NO, ind}'}$, percent/percent
		cal gas	dil gas	y_{NO}' ppm	z_{dil}' percent				
13	N ₂ ↓	982.5	21.5	12.72	2.14	12.71	-0.01	0.01	
		986.5	14.2	12.82	1.42	12.79	-.03	-.01	
	O ₂ ↓	986.5	31.7	12.60	3.11	12.59	-.01	.01	
		1002	39.4	12.51	3.78	12.49	-.02	.00	
	CO ₂ ↓	1002	28.6	12.64	2.78	12.62	-.02	.00	
		1002	19.5	12.75	1.91	12.73	-.02	.00	
	N ₂ ↓	1003	15.6	12.80	1.53	12.77	-.03	-.01	
		1002	37.2	12.53	3.58	12.48	-.05	-.03	
	CO ₂ ↓	989	29.8	12.62	2.93	12.39	-.23	-.21	-0.567
		982.5	21.0	12.73	2.09	12.55	-.18	-.16	-.603
90	N ₂ ↓	982.5	15.8	12.79	1.58	12.66	-.13	-.11	-.544
		989	34.3	86.98	3.35	86.91	-.07	.03	
	O ₂ ↓	992.5	21.6	88.08	2.13	87.98	-.10	.00	
		994	16.4	88.54	1.62	88.42	-.12	-.02	
	CO ₂ ↓	982.5	39.4	86.53	3.86	86.50	-.03	.07	
		997	29.8	87.22	2.90	87.14	-.08	.02	
	N ₂ ↓	998	21.2	88.13	2.08	87.97	-.16	-.06	
		998	16.3	88.55	1.61	88.45	-.10	.00	
	CO ₂ ↓	987.5	34.3	86.98	3.36	84.88	-2.10	-2.00	-.685
		992.5	25.1	87.78	2.47	86.39	-1.48	-1.38	-.636
		989	15.8	88.58	1.57	87.70	-.88	-.78	-.561

TABLE III. - INTERFERENCE OF WATER VAPOR

NO calibration gas concentration, ppm	Diluent gas	Flow rate, sccm		Calculated concentration		y _{NO,ind} ppm	Δy _{NO} = y _{NO,ind} - y _{NO,calc}	Δy' _{NO} ppm	i _F = $\frac{\Delta y'_{NO} \cdot 100}{y_{NO} z_{H_2O}}$, percent/percent	
		cal gas	dil gas	y _{NO} ppm	z _{H₂O} percent					
Carrier gas saturated at 68.4° C (p _{H₂O} = 218.0 torr); p = 764.5 torr, therefore, x _{H₂O,dil} = 0.2852										
13 ↓	N ₂ ↓	964	19.4	12.64	0.781	12.47	-0.17	-0.17	-1.72	
		982	19.7	12.74	0	12.75	.01	.01		
		958	19.5	12.64	.790	12.41	-.23	-.23	-2.30	
		1010	19.6	12.75	0	12.76	.01	.01		
		989	10.8	12.80	.429	12.67	-.13	-.13	-2.37	
		976.5	11.5	12.85	0	12.84	-.01	-.01		
90 ↓	N ₂ ↓	974	19.5	87.55	.777	85.77	-1.78	-1.68	-2.47	
		976.5	20.1	88.18	0	88.08	-.10	.00		
		967.5	19.7	87.51	.790	85.34	-2.17	-2.07	-2.99	
		992	20.3	88.20	0	88.09	-.11	-.01		
		982	11.6	88.54	.464	87.55	-.99	-.89	-2.17	
	O ₂ ↓	1002	20.3	87.52	.786	85.98	-1.54	-1.32	-1.92	
		995	20.4	88.19	0	87.97	-.22	.00		
Carrier gas saturated at 68.2° C (p _{H₂O} = 216.0 torr); p = 767.3 torr, therefore, x _{H₂O,dil} = 0.2815										
13 ↓	N ₂ ↓	1007	20.2	12.65	0.765	12.45	-0.20	-0.21	-2.17	
		1008	20.5	12.74	0	12.76	.02	.01		
		1008	20.1	12.65	.760	12.49	-.16	-.17	-1.77	
		990	43.25	12.25	1.613	11.77	-.48	-.49	-2.48	
		1002	45.45	12.44	0	12.44	.00	-.01		
		999	44.85	12.24	1.655	11.79	-.45	-.46	-2.27	
Carrier gas saturated at 68.4° C (p _{H₂O} = 218.0 torr); p = 765.3 torr, therefore, x _{H₂O,dil} = 0.2849										
13 ↓	N ₂ ↓	1002	20.8	12.74	0	12.77	0.03	0.01		
		998	20.4	12.64	.792	12.49	-.15	-.17	-1.70	
		995	46.4	12.42	0	12.43	.01	-.01		
		995	46.2	12.21	1.737	11.85	-.36	-.38	-1.79	
		995	42.3	12.47	0	12.41	-.06	-.02		
		995	41.8	12.29	1.581	11.92	-.37	-.33	-1.70	
90 ↓	O ₂ ↓	1000	21.5	12.73	0	12.71	-.02	.02		
		1005	21.5	12.62	.828	12.40	-.22	-.18	-1.72	
		982	21.7	88.05	0	87.72	-0.33	0.09		
		980	21.5	87.32	.848	85.41	-1.91	-1.49	-2.01	
		985	43.7	86.18	0	85.67	-.51	-.09		
		988	44.6	84.66	1.692	80.93	-3.73	-3.31	-2.31	
	N ₂ ↓	998	47.2	85.94	0	85.98	.04	.02		
		982	46.3	84.43	1.762	81.40	-3.03	-3.05	-2.05	
		998	22.3	88.03	0	88.03	.00	-.02		
		998	21.8	87.33	.844	85.80	-1.53	-1.55	-2.10	

significant, and therefore the best value is the overall mean or 0.60 ± 0.04 , where the error bounds represent the average of the absolute values of the deviations about the mean. In table III for water vapor, the mean value of i_F for the 13-ppm nitric oxide runs is -2.00, whereas that for the 90-ppm nitric oxide runs is -2.25. Again, this difference is not statistically significant, and therefore the best value is -2.1 ± 0.3 . This relatively large interference factor implies that water vapor is particularly effective as a third body in quenching NO_2^* – almost four times as effective as carbon dioxide.

The significance of these interference factors, particularly with respect to water vapor, can be illustrated by considering the following. Suppose that a gas sample saturated with water at room temperature is to be analyzed for nitric oxide. Since the water-vapor concentration is on the order of 2.5 percent, the error which would be introduced into the measurement of the nitric oxide concentration by not properly accounting for the water content would be about 5.3 percent. Particularly large errors could be incurred if the water vapor in the sample were at a much higher concentration than 2.5 percent – such a condition might occur in the hot gases produced from the combustion of hydrocarbons – and if this water were kept in the vapor state by transferring the sample to the low-pressure zone of the C/L-A by means of heated transfer lines. Removal of water by condensation, and particularly by desiccation, however, should be avoided because of possible removal of nitric oxide, nitrogen dioxide, or possibly even other gases in the sample. The use of selective membrane driers specific for water vapor may be one possible approach, but these need to be carefully evaluated for their selectivity to water only while in the presence of other gases in the sample stream, and even then, the quantity of water removed must be accurately known so that the final measured nitric oxide concentration can be appropriately adjusted for this water removal. One particularly attractive approach to handling a sample with a very high water content is to dilute the sample with a sufficient quantity of nitrogen to lower the dewpoint below room temperature, and then to analyze this diluted sample. This procedure has the desirable feature that it considerably simplifies sample handling and transfer while reducing the magnitude of the correction which must be applied for water vapor interference and also for interference from other gases, such as carbon dioxide which may be present. However, this dilution approach requires a sufficiently high nitric oxide concentration in the original sample to permit an accurate analysis after dilution (although in most cases this should not be a problem), and also an accurate measurement of the dilution ratio.

The interference factors measured in this study can be compared with interference factors which can be calculated from data of Niki, Warnick, and Lord (ref. 3) and discussion by Gilbert (ref. 3) obtained with early prototype C/L-A instruments and covering different nitric oxide and interfering species concentration ranges from those of the present study. (See table IV.) In view of the widely different concentrations represented, the interference factors agree well between the three studies, particularly for carbon dioxide.

The interference factors for water vapor appear possibly to depend on nitric oxide concentration; this dependence suggests the possibility of an interaction between water vapor and nitric oxide. However, because of the different sources of the data represented and also their limited nature, the existence of such a dependence cannot be certain. Nevertheless, it would probably be worthy of further study, especially if measurements of high concentrations of nitric oxide are required in the presence of water vapor.

TABLE IV. - COMPARISON OF INTERFERENCE FACTORS

Source	Carbon dioxide			Water vapor		
	z_{CO_2} , percent	y_{NO} , ppm	i_F	z_{H_2O} , percent	y_{NO} , ppm	i_F
Niki, et al. (ref. 3)	8.5	460 to 1995	^a -0.5	1.3	460 to 1995	^a -3.3
Discussion by Gilbert (ref. 3)	2.6 to 7.0	93	^a -0.7	2.6	194	^a -2.6
Present study	1.5 to 3.4	13 to 90	-0.6	0.8 to 1.8	13 to 90	-2.1

^aCalculated from data presented.

By way of illustration as to how the present interference factors can be used to correct an indicated nitric oxide concentration, equation (6) is first rearranged to give

$$y_{NO,act} = \frac{y_{NO,ind}}{1 + i_{FM}x_M}, \text{ where } M \text{ denotes } CO_2 \text{ or } H_2O. \text{ If both carbon dioxide and water}$$

$$\text{vapor are present, this expression can be rewritten as } y_{NO,act} = \frac{y_{NO,ind}}{1 + \sum_M i_{FM}x_M} \text{ since}$$

quenching of NO_2^* by more than one type of third-body molecule is the linear sum of the quenching effects from each type of molecule. (See ref. 2.) Then, for an assumed carbon dioxide concentration of 3 percent and a water vapor concentration of 2 percent, and an indicated nitric oxide concentration of 50 ppm, the actual nitric oxide concentration would be 53.2 ppm, or 6.4 percent higher than the indicated value.

CONCLUSIONS

The interference of small concentrations (less than 4 percent by volume) of oxygen, carbon dioxide, and water vapor on the analysis for oxides of nitrogen by chemiluminescence has been measured. The sample gas consisted primarily of nitrogen, with less than 100 parts per million concentration of nitric oxide, and with small concentrations of

oxygen, carbon dioxide, and water vapor added. From the analysis the following conclusions may be drawn:

1. In the analysis for nitric oxide by chemiluminescence, the presence of foreign gases in the sample, that is, those not present in the calibration gas, can interfere with the analysis and give an indicated nitric oxide concentration which is in error.

2. Interference factors relative to nitrogen have been determined for carbon dioxide at concentrations up to 3.5 percent and for water vapor at concentrations up to 1.8 percent. These interference factors, -0.6 and -2.1, respectively, agree well with interference factors calculated from data available in the literature over broader concentration ranges.

3. An interference factor for oxygen was determined to be virtually zero at oxygen concentrations up to 4 percent. This result suggests that the quenching efficiency of oxygen is very close to that of nitrogen.

Langley Research Center,

National Aeronautics and Space Administration,

Hampton, Va., May 19, 1975.

APPENDIX A

ADSORPTION OF NITRIC OXIDE AND NITROGEN DIOXIDE ON TEFLON AND STAINLESS STEEL

Since both teflon and stainless steel are used extensively in the experimental apparatus as well as in the C/L-A instrument itself, a separate experiment was conducted to measure the adsorption characteristics of nitric oxide and nitrogen dioxide on these materials. A schematic of the flow system is shown in figure 2. The test section con-

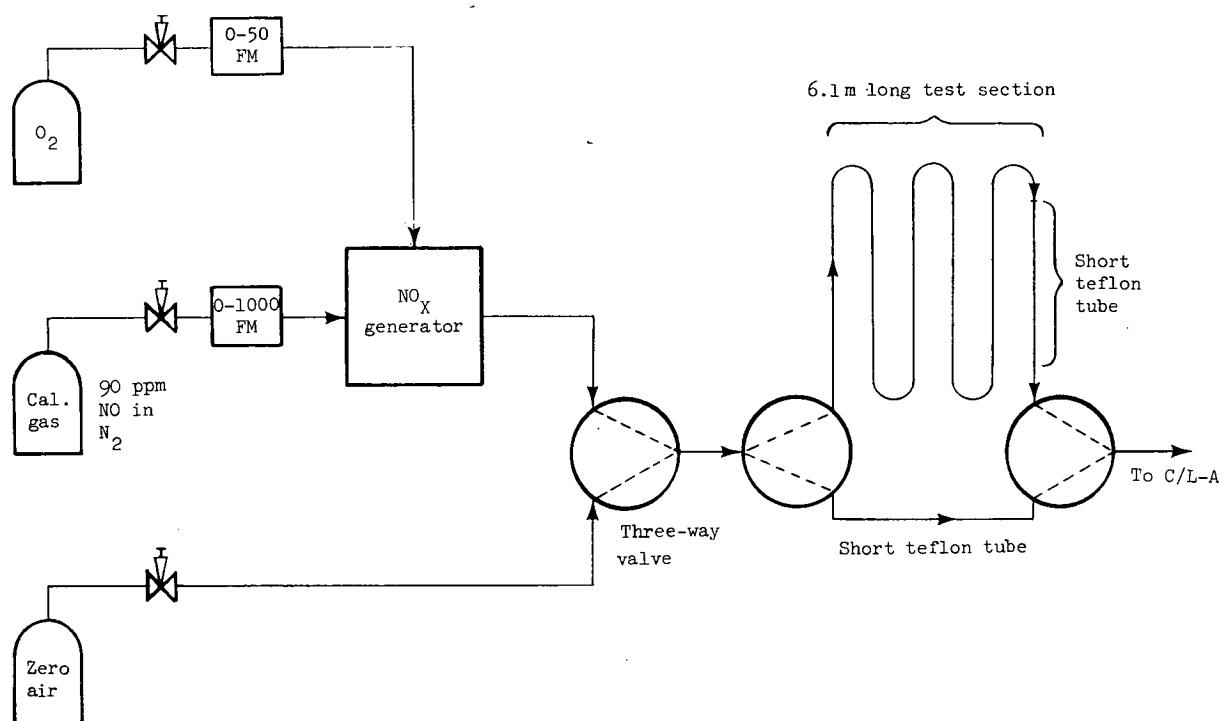


Figure 2.- Flow system for adsorption studies.

sisted of a teflon or stainless-steel tube, 6.1 m long by 0.3175 cm outside diameter. Nitric oxide calibration gas (90 ppm in all these tests) was first run through the short teflon tube to establish the steady-state reading by the C/L-A. The flow was then switched through the test section until the C/L-A reading reached the previously established steady-state reading, after which time the calibration gas was shut off and the test section purged with zero air. From these data, rise times and decay times were measured. Since the teflon tubing had a thicker wall and thus a smaller internal surface area than the stainless-steel tubing (about 309.7 cm² for teflon as compared with 438 cm² for stainless steel), the observed rise times and decay times were normalized on a per unit area basis. The

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results are shown in Table V. These data show that although nitric oxide saturates teflon faster than stainless steel, it desorbs slower.

TABLE V. - ADSORPTION CHARACTERISTICS FOR 90 ppm
NITRIC OXIDE IN NITROGEN

Tube material	Rise time to approximately steady state, min/cm ²	Decay time to 0.1 percent of original steady-state value, min/cm ²
Teflon	0.0026	0.0051
Stainless steel	.0034	.0031

TABLE VI. - ADSORPTION CHARACTERISTICS FOR 55 ppm NITROGEN DIOXIDE
(AT 89.6 ppm NO_x) IN NITROGEN

Tube material	Rise time to approximately steady state, min/cm ²		Decay time to 0.1 percent of original steady-state value, min/cm ²	
	NO ₂	NO _x	NO ₂	NO _x
Teflon	(a)	(a)	0.039	0.033
Stainless steel	0.050	0.050	.022	.020

^aNot measured.

For determining the adsorption characteristics of nitrogen dioxide, nitrogen dioxide was generated by reacting nitric oxide calibration gas with ozone in a modified form of the ThermoElectron Corporation Model 100 NO_x Generator. Modifications consisted of the addition of fine-control flow valves and two linear mass flowmeters for measuring the flow rates of the nitric oxide calibration gas and the oxygen to the NO_x generator. For a nitric oxide calibration gas concentration of 90 ppm and a flow rate of approximately 1000 sccm, the oxygen flow rate was 3.2 sccm. This was low enough to prevent all the nitric oxide from being oxidized to nitrogen dioxide, and thus insured that no free ozone existed in the sample gas. The concentration of the nitrogen dioxide thus generated was determined from the difference between the readings of the C/L-A in the NO_x and NO modes, and was about 55 ppm. Rise times and decay times, determined in a manner similar to those for nitric oxide, are shown in table VI. When these data are compared with those in table V, it is seen that nitrogen dioxide adsorbs much more strongly on both teflon and stainless steel than does nitric oxide. Furthermore, both nitric oxide and nitro-

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gen dioxide adsorb more strongly on teflon than on stainless steel, a result which agrees with the findings of Healy and Urone (ref. 4) in their study of nitrogen dioxide adsorption. However, since the differences in adsorption between teflon and stainless steel are relatively small, in ordinary circumstances there would be no reason to prefer stainless steel to teflon. This is particularly true if (1) separate lines are used to transfer sample gas and calibration gas to the C/L-A, (2) the nitric oxide concentrations in the transfer lines are not subject to sudden, large changes, and (3) the calibration gas concentrations are close to the sample gas concentrations.

APPENDIX B

DECONDITIONING OF THE STAINLESS-STEEL CONVERTER COIL AND IMPLICATIONS WITH REGARD TO THE MEASUREMENT OF NITROGEN DIOXIDE CONCENTRATIONS

When using the stainless-steel converter coil with gas samples low in oxygen concentration, deconditioning of the coil can easily occur. Deconditioning is readily apparent when the C/L-A reading in the NO_x mode is lower than that in the NO mode; thus, less nitric oxide plus nitrogen dioxide in the sample than nitric oxide alone is indicated – an obvious impossibility. A deconditioned coil can be reconditioned relatively easily by flowing approximately 50 sccm ozone through the coil in a stream of 950 sccm nitrogen for about one-half hour, followed by an air purge of the system for several hours, or until stable (that is, nondrifting) C/L-A readings are attained. Once conditioned, the converter coil can be maintained in this state for at least 1 week, even when running samples low in oxygen, by leaving room air flushing the coil (at its 800° C operating temperature) when the C/L-A is on standby.

Even with a completely conditioned converter coil,¹ however, the presence of oxygen in the sample can cause the indicated concentration for nitric oxide to be very slightly lower in the NO_x mode than in the NO mode. To determine the extent of this effect, the following experiment was run. Calibration gas consisting of 90-ppm nitric oxide in nitrogen was passed through a cold trap at dry-ice temperature to remove any possible nitrogen dioxide contamination and then flow-diluted with oxygen and analyzed for nitric oxide in both the NO and NO_x modes. Results are shown in table VII. The observed errors in the readings in the NO_x mode, shown in the last column, are of particular significance in the measurement of nitrogen dioxide concentrations. Since the concentration of nitrogen dioxide is obtained by difference from the C/L-A readings in the NO and NO_x modes, even small errors in the NO_x-mode readings caused by the presence of oxygen in the sample must be appropriately accounted for.

It should be pointed out that these observations are for the stainless-steel converter coil operating at a pressure close to that in the nitric oxide plus ozone reactor, that is, about 5 to 8 torr, instead of at the usual near-atmospheric pressure. This lower pressure in the converter coil resulted from a modification to the original flow system of the Model 12A in which the sample flow-control capillaries were relocated external to the main instrument cabinet to make them more accessible for easy inspection and cleaning. Whether the observed problems (of slow catalyst deconditioning and of oxygen affecting

¹That is, one in which the indicated concentration for the analysis of nitrogen-dioxide-free nitric oxide calibration gas in nitrogen is identical in the NO and NO_x modes.

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the indicated nitric oxide concentration in the NO_X mode) are peculiar to this lower pressure operation is not known.

TABLE VII. - EFFECT OF OXYGEN ON ANALYSIS FOR NITRIC OXIDE IN NO_X MODE

Calibration gas flow rate, sccm	Oxygen diluent flow rate, sccm	Oxygen concentration, percent	$(y_{\text{NO,NO}_X \text{ mode}} - y_{\text{NO,NO mode}}) 100$
			$y_{\text{NO,NO mode}}$ percent
1000	0	0	0
980	30	3.0	-.37
980	199	18.5	-.52
995	20	2.0	-.22

In any event, in measuring nitrogen dioxide concentrations there is always the additional complication that converter efficiencies are less than 100 percent, and hence, they too must be determined and properly accounted for. And, because the nitrogen dioxide concentration in a sample is often only a small fraction of the total concentration of oxides of nitrogen, the omission of even small corrections can introduce relatively large percentage errors into the measurement. Attempts to avoid making such corrections by calibrating the C/L-A in the NO_X mode by using nitrogen dioxide calibration gas diluted with oxygen are probably best avoided because of the inherent instability of nitrogen dioxide. Because of the several uncertainties and corrections required, measurement of nitrogen dioxide concentrations by C/L-A should be considered approximate.

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